



ARL-TR-7225 • MAR 2015



US Army Research Laboratory

Hydrolytic Stability Study of Tetranitroglycoluri (TNGU) Produced via the US Army Research Laboratory's Synthetic Method

by William M Sherrill, Eric J Bukowski, and Terry L Piatt

Approved for public release; distribution is unlimited.

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.



Hydrolytic Stability Study of Tetranitroglycoluri (TNGU) Produced via the US Army Research Laboratory's Synthetic Method

by William M Sherrill, Eric J Bukowski, and Terry L Piatt
Weapons and Materials Research Directorate

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
<p>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) March 2015		2. REPORT TYPE Final		3. DATES COVERED (From - To) 12 Oct 2012	
4. TITLE AND SUBTITLE Hydrolytic Stability Study of Tetranitroglycoluril (TNGU) Produced via the US Army Research Laboratory's Synthetic Method				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) William M Sherrill, Eric J Bukowski, and Terry L Piatt				5d. PROJECT NUMBER AH43	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Research Laboratory ATTN: RDRL-WML-C Aberdeen Proving Ground, MD 21005-5066				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-7225	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Tetranitroglycoluril (TNGU) was prepared according to the US Army Research Laboratory's (ARL's) method by the nitration of imidazo-[4,5-d]-imidazole nitrate using trifluoroacetic anhydride and 100% nitric acid. This resulting material was then subjected to hydrolytic stability studies in which it was placed into a temperature and humidity chamber set to 23 °C and 85% relative humidity and the change in concentration of TNGU was measured over time through the use of nuclear magnetic resonance spectroscopy.					
15. SUBJECT TERMS tetranitroglycoluril, TNGU, hydrolytic stability					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 18	19a. NAME OF RESPONSIBLE PERSON William M Sherrill
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 410-278-8608

Contents

List of Figures	iv
List of Tables	iv
Acknowledgments	v
1. Introduction	1
2. Hydrolytic Stability Studies	2
3. Experimental	4
3.1 Preparation of TNGU According to the ARL Method	5
3.2 Hydrolytic Stability Studies	5
4. Conclusions	5
5. References	7
List of Symbols, Abbreviations, and Acronyms	9
Distribution List	10

List of Figures

Fig. 1	Molecular structures of TNGU and HMX	1
Fig. 2	Potential mechanism of hydrolytic decomposition of TNGU	1
Fig. 3	Stacked plot of NMR change in concentration over time.....	3
Fig. 4	Plot of change in concentration of TNGU over time showing all points..	4
Fig. 5	Change in concentration of TNGU over time with statistical outliers removed.....	4

List of Tables

Table	Change in concentration values over time as determined via nuclear magnetic resonance (NMR) analysis	2
-------	--	---

Acknowledgments

The authors wish to thank Mr Eric Johnson and Ms Lori Pridgeon for general equipment assistance and supply management. The authors also wish to thank Drs Joseph Banning, Jesse Sabatini, Brian Roos, Thuvan Piehler, Chase Munson, and Mr Stephen Aubert for procedural input and technical review.

INTENTIONALLY LEFT BLANK.

1. Introduction

Tetranitroglycoluril (TNGU or **1**) (which is also known as Sorguyl) is an energetic material first described in open literature by the French in 1975.¹⁻⁴ This material has a predicted performance comparable to the standard military explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX or **2**) (see Fig. 1), but unfortunately suffers from hydrolytic instability and until recently was often considered too sensitive to be safely handled on the large scale.⁵ Recent efforts to stabilize the material through substitution at the bridgehead positions did not result in material that was appreciably more stable than the parent species.^{6,7} However, it was found that material synthesized through an alternative route exhibited small-scale sensitivity numbers that were significantly improved over that produced via the literature routes to **1**.⁸⁻¹⁰

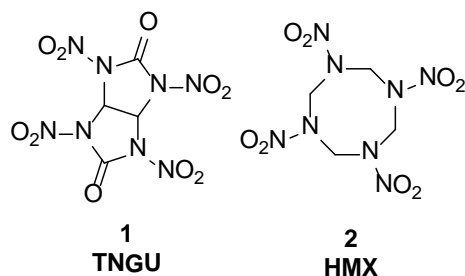


Fig. 1 Molecular structures of TNGU and HMX

The origin of the hydrolytic stability of the molecule comes from the dinitrourea moiety, which is present in both of the fused 5 membered rings of the molecule. The presence of 2 nitro groups α to the carbonyl activates the carbonyl to nucleophilic attack by water. This is expected to result in ring opening and ultimately decarboxylation to yield a final product of TNGU (see Fig 2).¹¹

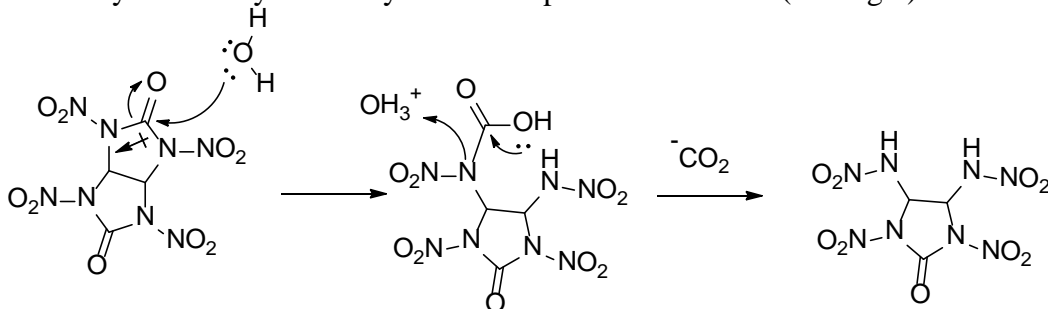


Fig. 2 Potential mechanism of hydrolytic decomposition of TNGU

According to a Strategic Environmental Research and Development Program (SERDP) study conducted by the Department of the Navy, the half-life of **1** prepared via the nitration of glycolurils utilizing a mixture of 100% nitric acid (HNO₃) and acetic anhydride (Ac₂O), when exposed to an atmosphere of 85% relative humidity (RH) and 23 °C was 3.67 days.^{12,13} This result was the baseline that was used to compare the hydrolytic stability of the material produced according to the US Army Research Laboratory's (ARL's) synthetic method.

With ARL's new method of the synthesis of **1** producing material with a significantly different sensitivity profile, it was postulated that the hydrolytic stability of the material may have also been appreciably altered through the modification of the synthetic methodology. To this end the hydrolytic stability of material produced according to the ARL method was compared to the Navy's previously published work on the hydrolytic stability of **1**.¹²

2. Hydrolytic Stability Studies

Using the method outlined in the Navy study, **1** prepared using the ARL method was subjected to environmental conditioning in a temperature and humidity controlled chamber set to 23 °C and 85% RH.

By taking 50-mg samples of **1** and subjecting them to the temperature and humidity (T&H) chamber for the predetermined period of time then dissolving them in acetone-d₆, it was possible to measure the change in concentration of the samples over time (refer to the Table and Fig. 3).

Table Change in concentration values over time as determined via nuclear magnetic resonance (NMR) analysis

Sample No.	Mass (mg) ^a	Time (h) ^b	Ratio of A _x ^d to A ₀ ^e	Measured Concentration (M) ^c
0	50.93	0	1.0000	0.2484
1	50.48	16	0.8182	0.2032
2	50.61	20	0.6338	0.1574
3	50.74	24	0.6618	0.1644
4	50.72	40	0.4500	0.1118
5	50.4	44	0.3879	0.0963
6	50.66	48	0.4245	0.1054

^amilligram; ^bhour; ^cmole; ^dconcentration at time X; ^econcentration at time 0.

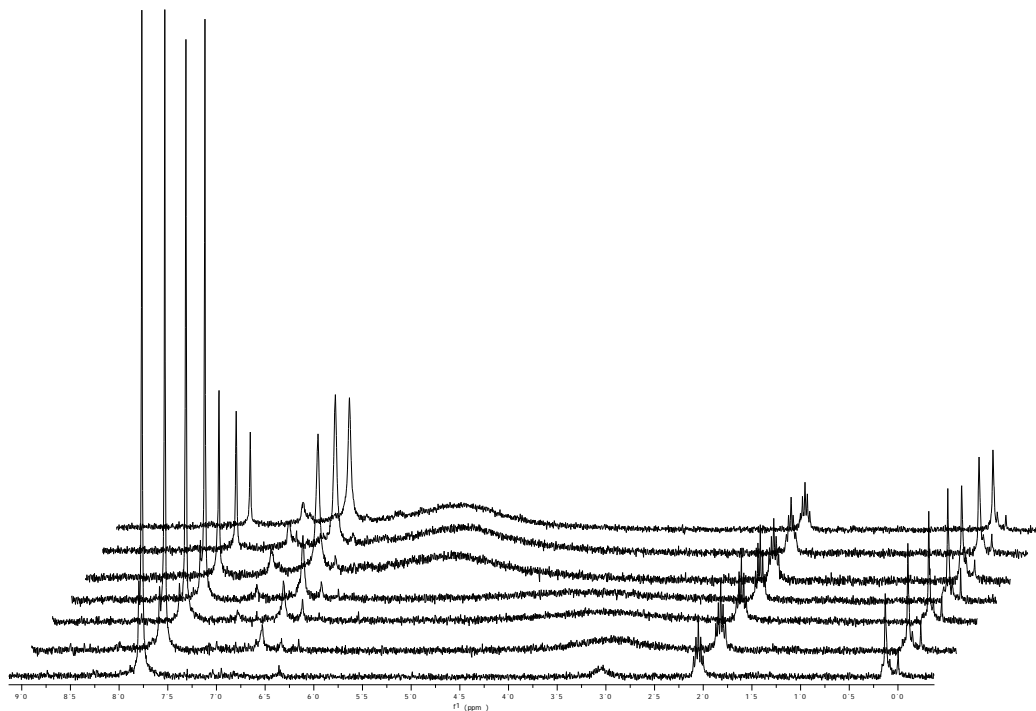


Fig. 3 Stacked plot of NMR change in concentration over time

Concentration as a function of time was then plotted resulting in the graph shown in Fig. 4, which exhibits a linear decrease in concentration indicative of zero order reaction kinetics. The zero order rate law equation is shown in Eq. 1

$$\text{Rate} = k[A]^n \quad (1)$$

where k is the rate constant and A is the concentration of **1**, can be plotted to generate a line, the slope of which is equal to k for the reaction. Plotting the data shown in the table gives a k value of 0.0035 moles per second (M/s).

Using the zero order half-life equation shown in Eq. 2,

$$t_{1/2} = \frac{[A]_0}{2k} , \quad (2)$$

where the initial concentration is 0.2484 M results in a half-life of the reaction of 35.5 h.

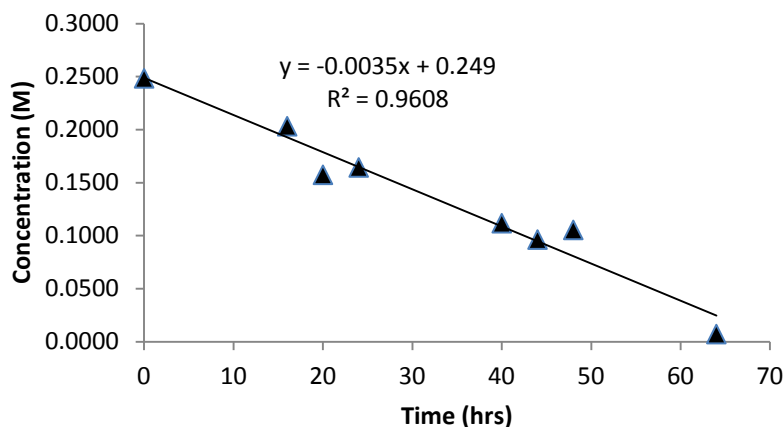


Fig. 4 Plot of change in concentration of TNGU over time showing all points

Looking at the entire data set, there are 2 points that are statically outside of the rest of the data. By removing those outlying 2 points, it is possible to increase the trend line correlation increases from 0.96 to 0.99. Doing this changes the slope of the line slightly, which slightly increases the measured rate constant of the reaction making the new half-life 32.7 h (Fig. 5), an 8% decrease.

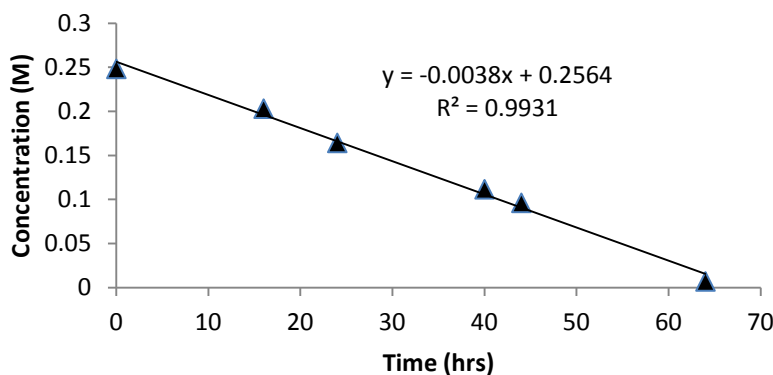


Fig. 5 Change in concentration of TNGU over time with statistical outliers removed

3. Experimental

NMR experiments were completed using an Anasazi Instruments 90-megahertz (MHz) NMR. The temperature and humidity chamber used in the experiment was a Thermotron Model SM-8-3800 set to hold 23 °C and 85% RH at <1% parameter variance. All chemicals were obtained from Sigma-Aldrich, St. Louis, Missouri and were used as received.

Note: While this compound was prepared without incident according the following procedures, this material is energetic and should be prepared and handled cautiously by trained personnel.

3.1 Preparation of TNGU According to the ARL Method⁸⁻¹⁰

A total mass of 1.04 grams (g) (4.08 millimoles [mmol]) of nitrate salt was dissolved into 20 milliliters (mL) of 100% HNO₃ at 0 °C under a nitrogen (N₂) atmosphere. To this solution was added, by drops, 20 mL of trifluoroacetic anhydride (TFAA) at a rate to keep the temperature under 10 °C. Upon completion of the addition, the material was allowed to warm to ambient temperature and stirring was continued for 2 h. After the time had elapsed, the suspension was cooled to 0 °C, stirring was stopped and the suspended solid was allowed to settle. The mother liquor was decanted, and the remaining solid was washed with dichloromethane (DCM) (5 × 20 mL). The material was then vacuum dried (10 torr 20 °C) for 2 h. The total amount of **1** recovered from this process was 0.95 g (2.93 mmol, 72%)

Peak decomposition was observed to be 217–220 °C in the DSC. ¹H NMR (600.182 MHz, Acetone-D₆) δ 7.78 (s, 2H); ¹³C NMR (150.046 MHz, Acetone-D₆) δ 141.8, 65.3; Fourier transform infrared (FTIR) (DATR), $\tilde{\nu}$ = 2997, 2894, 1798, 1652, 1617, 1594, 1255, 1144, 1090, 768, 730, 698; C₄H₂N₄O₁₀: calcd C 14.92; H 0.63; N 34.79%; found: C 14.89; H 0.63; N 34.72%.

3.2 Hydrolytic Stability Studies

Twelve samples of approximately 50 mg each of **1** were placed into open vials, and then placed into the Thermotron T&H chamber set to 23 °C and 85% RH. The vials were removed at selected time intervals (refer to the Table) and then diluted with 500 µL of acetone-d₆ and immediately placed into the NMR for analysis. Using the solvent peak at 2.05 parts per million (ppm) as the internal standard with an integration value of 1, the change in concentration of the bridgehead hydrogens at 7.78 ppm over time was plotted and the resulting data shown in the Table as well as the graph shown in Fig. 4.

4. Conclusions

TNGU produced by ARL's new method has a half-life of between 32.7 and 35.5 h at 23 °C and 85% RH. This appears to be appreciably shorter than the 88.1 h of TNGU, which has been produced and tested by the Navy. It should also be noted that while the results of the T&H chamber study indicate a zero order reaction for the decomposition of the **1** produced via ARL method, the hydrolysis study conducted by the Navy yielded a sigmoidal concentration curve. Part of the discrepancy may be due to the method used by the Navy for their humid air hydrolysis in which a saturated potassium chloride solution was placed into a

desiccator was employed to reach the desired humidity. Use of the T&H chamber allows for highly accurate control of temperature and humidity conditions in the chamber (<1% deviation) over the duration of the test resulting in a significantly higher environmental control. In order to get a truly accurate comparison of the hydrolytic stability of the materials, the T&H chamber test will be repeated using material prepared according to the literature procedures, and will be released in an upcoming report. The results of the current experiment indicate that although **1** obtained from the ARL synthetic method does exhibit a marked decrease in sensitivity to external insult, it still is unstable in the presence of water and still requires handling and storage in environments where care has been taken to minimize exposure to atmospheric moisture. These results also indicate the origin of the stability of ARL's **1** is most likely due to differences in the morphology of the material obtained from the new method.

5. References

1. Boileau J, Emeury JML, Kehren JPA. Tetranitroglycoluril for explosives, Ger. Offen. 2,435,651, Société Nationale de Pouders et Explosifs, Paris, France, 1975.
2. Boileau J, Emeury JML, Kehren JPA. tetranitroglycoluril and method of preparation thereof. US Patent 4,487,938, Société Nationale des Poudres et Explosifs, Paris, France, 1984.
3. Boileau J, Carail M, Wimmer E, Gallo R, Pierrot M. Dérivés nités acétylés du glycoluril. *Propellants Explos. Pyrotech.* 1985;10:118–120.
4. Boileau J, Wimmer E, Carail M, Gallo R. Méthodes de préparation de dérivés nités et nitroacétylés du glycoluril (I), *B. Soc. Chim. Fr.* 1986;3, 465–469.
5. Sherrill WM, Banning JE. Preparation of a spherical morphology of tetranitroglycoluril (TNGU). Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 May. Report No.: ARL-TR-6940. Also available at:
http://www.arl.army.mil/www/default.cfm?technical_report=7078
6. Sherrill WM, Johnson EC, Paraskos AJ. Synthesis and characterization of mono-, di-, and tetranitrated 7,8-disubstituted glycolurils. *Propellants Explos. Pyrotech.* 2014;39:90–94.
7. Sherrill WM, Johnson EC, Paraskos AJ. Synthesis and characterization of mono-, di-, and tetranitrated 7,8-disubstituted glycolurils. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Feb. Report No.: ARL-RP-474. Also available at:
http://www.arl.army.mil/www/default.cfm?technical_report=7043
8. Sherrill, WM, Johnson EC, Banning JE. A method for the synthesis of tetranitroglycoluril from imidazo-[4,5-d]-imidazoles with loss of dinitrogen oxide. *Propellants Explos. Pyrotech.* 2014; 39:670–676.
9. Sherrill WM, Johnson EC, Banning JE. A method for the synthesis of tetranitroglycoluril from imidazo-[4,5-d]-imidazoles with loss of dinitrogen oxide. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Dec. Report No.: ARL-RP-0515.

10. Sherrill WM, Johnson EC, Banning JE. A new method for the synthesis of tetranitroglycoluril from imidazo-[4,5-d]-imidazoles with loss of dinitrogen oxide. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Feb. Report No.: ARL-TR-6829. Also available at:
https://www.arl.army.mil/www/default.cfm?technical_report=7023
11. Lee YW, Goede P, Latypov N, Ostmark, H. Synthesis and Analysis of N,N',N'',N'''-tetranitro-1,1,2,2-ethanetetramine and Energetic Salts Thereof. Proceedings of NTREM 2006, Pardubice, Czech Republic, Pg 124-1, 2006.
12. Chapman RD, Quintana RL, Baldwin LC, Hollins RA. Cyclic Dinitroureas as Self-Remediating Munition Charges. Final Report SERDP Project WP-1624, 2009 Feb.
13. Merritt AR, Hoang HQ, Young KJ, Baldwin LC, Ferguson BP, Chapman RD, Quintana RL. Self remediating explosives based on tetranitroglycoluril (TNGU). 5th JANNAF Combustion, 33rd Airbreathing Propulsion, 33rd Exhaust Plume and Signatures, 27th Propulsion Systems Hazards Joint Subcommittee Meeting, Monterey (CA) 2012 Dec 3–6.

List of Symbols, Abbreviations, and Acronyms

[A]	concentration of TNGU or 1
Ac ₂ O	acetic anhydride
ARL	US Army Research Laboratory
DCM	dichloromethane
FTIR	Fourier transform infrared
g	gram
h	hour
HMX (or 2)	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HNO ₃	nitric acid
<i>k</i>	rate constant
M	mole
M/s	moles per second
mg	milligram
MHz	megahertz
mL	milliliter
N ₂	nitrogen
NMR	nuclear magnetic resonance
ppm	parts per million
RH	relative humidity
SERDP	Strategic Environmental Research and Development Program
<i>t</i> _{1/2}	half-life
TFAA	trifluoroacetic anhydride
TNGU (or 1)	tetranitroglycoluril
T&H	temperature and humidity

1 DEFENSE TECHNICAL
(PDF) INFORMATION CTR
DTIC OCA

2 DIRECTOR
(PDF) US ARMY RESEARCH LAB
RDRL CIO LL
IMAL HRA MAIL & RECORDS
MGMT

1 GOVT PRINTG OFC
(PDF) A MALHOTRA

2 WEAPONS DEV &
(PDF) INTEGRATION
DIRCTRT AMRDEC
RDMR WDN
J NEIDERT
G DRAKE

1 US ARMY ARDEC
(PDF) AMSRD AAR AEE W
R DAMAVARAPU

1 PICATINNY ARESENAL
(PDF) RDAR MEE W
A PARASKOS

1 LOS ALAMOS NATL LAB
(PDF) D CHAVEZ

1 LAWRENCE LIVERMORE
(PDF) NATL LAB
P PAGORIA

2 NAVAL SURFACE WARFARE
(PDF) CTR
B SLEADD
P CARUANA

13 DIR USARL
(PDF) RDRL CI
P PLOSTINS
RDRL WM
P BAKER
B FORCH
RDRL WML
M ZOLTOSKI
RDRL WMM
J ZABINSKI
RDRL WML B
E BYRD
B RICE
N TRIVEDI
RDRL WML C
S AUBERT
K MCNESBY
B ROOS
W SHERRILL
RDRL WML H
J NEWILL